INTEGRATED MICROCHEMICAL ANALYSIS SYSTEM USING DS2 PENETRATOR TECHNOLOGY FOR THE ENANTIOMERIC DETECTION OF AMINO ACIDS

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Any strategy for investigating whether abiotic and/or biotic organic molecules are present on Mars and the search for biosignatures should focus on compounds which are readily synthesized under plausible prebiotic conditions, play an essential role in biochemistry as we know it and have properties such as chirality (handedness) which can be used to distinguish between abiotic vs. biotic origins (1). Amino acids are one of the few compound classes that fulfill all these requirements. They are synthesized in high yields in prebiotic simulation experiments, are one of the more abundant types of organic compounds present in carbonaceous meteorites and only the L-enantiomers are used in the proteins and enzymes in life on Earth.

The results of the Viking Landers have suggested the presence of a hyperoxidizing layer which has denuded organic molecules from the soil near the surface. While several experiments have been proposed to confirm the existence of such a layer and to establish its spatial extent, models based on the diffusion into the soil of reactive oxidants formed at or near the surface (2) suggest that this layer is less than 3 meters thick. In the following, we describe the modification of the DS2 Penetrator technology to incorporate an integrated microchemical analysis system using capillary electrophoresis which can detect the presence of amino acids in a subsurface soil sample and resolve the ratios of L- and D-enantiomers with orders of magnitude more sensitivity than the Viking Gas Chromatograph - Mass Spectrometer.

In our proposed implementation, we plan for three stages of increasing complexity. In each case, the DS2 drill sampling system will be used to provide a subsurface soil sample for analysis. Each implementation substitutes a science module for the existing H_2O package, with no additional changes to the DS2 geometry, power system, or supporting electronics except for the interface module. The simplest version, MOD or the Mars Organic Detector, consists of a sublimation analyzer with fluorescent detection of amines and polycyclic aromatic hydrocarbons (PAH's). This system is a modest extension of the existing DS2 water experiment, but adds Tunable Diode Laser capability for detection of CO_2 to the existing H_2O measurement, and a chemical detection system for amines and PAH's using UV excited fluorescence, which has a detection limit of femtomoles from a 0.5 cc sample. This configuration would provide highly sensitive detection of amino acids, free amines and amino acid decomposition products while independently detecting polycyclic aromatics and the presence of carbonates in the mineral matrix. All components of this system are

commercially available, or have been developed and demonstrated by ongoing technology developments.

The second stage of complexity, substitutes an integrated wet chemical analyzer, based on a microchip capillary electrophoresis system for the existing DS2 science module. The sample is again obtained by the existing drill sampling system, and placed in a heated crucible, and sealed from the ambient. Liquid is then added to the 0.2 to 0.4 cc. sample, and the soil is hydrolyzed at 145 °C for approximately 5 to 7 minutes. The liquid is then transferred into a microfluidics processing cell for desalting, labeling and concentrating. The sample is then injected into the chiral separation column for separation of amino acids and polycyclic aromatic hydrocarbons which are detected using UV fluorescence. The microimplementation of this separation procedure using microchip capillary electrophoresis (CE) has been demonstrated through our PIDDP effort by extension of recent developed CE methods (3). Enantiomeric resolution of the majority of the amino acids found in carbonaceous meteorites has been obtained in less than 2 minutes using cyclodextrin as the chrial separation medium. The microfluidics/ CE analysis system consists of a stack of wafer scale components which individually provide the liquid flow channels, the capillary separation zones, the electrophoretic controls, the fluid logic and the detection system. Temperature control is maintained by a thermal generator. The anticipated time required to process one soil sample, execute up to 10 replicate chiral separations and perform three calibrations is approximately one hour.

In the third stage of complexity, we add a miniaturized Raman spectrometer to the stage II system. This system, based on commercial components modified for flight, will use UV laser excitation, fiber optic probes with integrated high and low pass filters, and a photodiode array spectrometer. The UV laser will be used as part of the CE detection system. Fiber optic probes are placed along the sidewall of the penetrator body, to monitor the chemical composition of the soil being sampled by the CE system. We will specifically look for the presence of carbonate, phosphate, sulfate and hope to resolve hydrated silicas, as well as a number of transition metal environments in the soil matrix. The Raman system will have a resolution of better than 30 cm^{-1} and will cover the spectral range of 300 to 2400 wavenumbers, and uses a proprietary fiber technology to focus on material less than 1 mm. from the end of the fiber, and to achieve gain enhancements of up to a factor of 7 over competing approaches. The fibers will be embedded in the penetrator body for shock resistance.

In the presentation, we will provide an overview of our results demonstrating the high performance of CE based chiral separation on microchips in comparison to capillary separations and traditional HPLC analyses. We will show preliminary drawings demonstrating the proposed science modules for stages I, II and III of the concept, and showing the integration of the modified DS2 probe. If time permits, we will discuss the microfluidics technology and several engineering details addressed by the team.

References cited:

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